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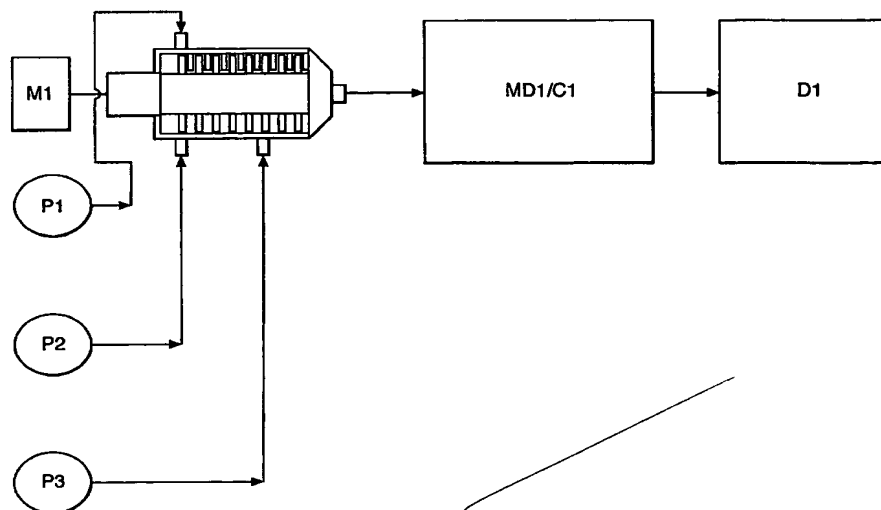
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[Continued on next page]

(54) Title: ALGINATE OR LOW-METHOXY PECTATE GEL



(57) Abstract: Our invention provides a highly convenient process and equipment which can be used to prepare alginate or low-methoxy pectate gels on site e.g. where the product is to be used. The process comprises making a sol in an in-line dynamic mixer, then introducing gelling ions, e.g. calcium ions, into the sol in the mixer and immediately subsequently allowing the sol to gel. The equipment consists of an in-line dynamic mixer with feed points for the alginate or low-methoxy pectate and water spaced sufficiently apart from a feed point for a source of gelling ions such that the sol is formed before it comes into contact with the gelling ions. The process can be used to prepare gelled particles for use as feed for live stock as well as to produce gels containing e.g. meat or fruit. A particular use is to produce feed containing sensitive ingredients e.g. live bacteria.

WO 03/088767 A1

WO 03/088767 A1



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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## ALGINATE OR LOW-METHOXY PECTATE GEL

Alginate gels are well-known as are methods for their  
5 preparation by converting alginate in its sodium salt form,  
as a sol, into a gel by action of calcium ions.

Alginate gels have been used as foodstuffs e.g.  
petfoods, with meat in alginate gel, and simulated fruits,  
with pureed fruit in alginate gel.

10 Alginate sols are usually in the form of the sodium  
salt but other cations can be used to form sols. (Note that  
an inherent characteristic of an alginate sol is that the  
alginate is hydrated.) Similarly calcium ions are usually  
the cations that are used as gelling ions to convert such  
15 sols to gel form but other cations can be used. It is  
well-known that low-methoxy pectate behaves like alginate.  
For simplicity's sake we describe the background to our  
process and products in terms of sodium alginate and use of  
calcium ions to gel the sol but the use of low-methoxy  
20 pectate and other cations must always be borne in mind.

Broadly speaking there are three methods of converting  
an aqueous sol of sodium alginate to a gel. The first is  
by diffusion of calcium ions into an aqueous sol of sodium  
alginate. The second is by diffusion of hydrogen ions i.e.  
25 from an acid into an aqueous sol of sodium alginate  
containing a calcium salt the solubility of which is  
greatly increased by the hydrogen ions. The third is by  
mixing an aqueous sol of sodium alginate with a source of

soluble calcium ions and allowing the mixture to gel without further mixing.

To obtain good quality gels it is well-known to be important that gelation occurs as far as possible in the  
5 absence of shear.

The third method has the major disadvantage over the other two methods that the sodium alginate sol is mixed with a source of soluble calcium ions and shearing at least at the start of gelation is unavoidable. All the methods  
10 of preparing acceptable gels have involved use of relatively complex systems and have required skills above that of an untrained person. We have invented a process and related equipment by which the third method can be used to prepare acceptable gels and in particular gel pieces  
15 with especially useful characteristics, even without the use of complex systems.

In a particular form of our invention our process and related equipment and products can be used for delivering therapeutic amounts of biologically active substances to  
20 humans and, in particular, to livestock.

An aspect of our invention is that we have discovered that alginate and low-methoxy pectate sols can advantageously be produced by adding a dispersion of alginate or low-methoxy pectate to water in an in-line  
25 dynamic mixer. Therefore our invention, in this aspect, provides a process for preparing an alginate or low-methoxy

pectate sol in which a dispersion of alginate or low-methoxy pectate is mixed with water in an in-line dynamic mixer.

In a further and particularly important aspect of our invention we provide a process for preparing an alginate or low-methoxy gel in which water and a dispersion of alginate or low-methoxy pectate are mixed in an in-line dynamic mixer to produce a sol of alginate or low-methoxy pectate in the mixer and then free gelling ions are generated in the sol in the in-line mixer either a) by including in the water or in the dispersion of alginate or low-methoxy pectate a salt providing gelling ions when dissolved which salt is insoluble at neutral pH but soluble at acid pHs and by feeding an acid to the sol as an aqueous solution or as a dispersion or b) by feeding a dispersion of a salt providing gelling ions to the sol after which the resulting mixture is allowed to gel. (When option a) is used the salt insoluble at neutral pH is preferably included in the dispersion of alginate or low-methoxy pectate.)

Our process is particularly advantageous in that it provides a simple process for preparing alginate or low-methoxy pectate gels. It provides a process in which sols do not need to be prepared in advance. Preparation in advance inherently leads to the risk that not all the sol prepared will be needed. The sol is produced in-line, i.e. continuously. There is a major advantage in that our

process does not involve use of vessels to store sols.

Cleaning of such vessels is a major task. Our process also has the major advantage that it uses minimal and simple equipment which can be operated without complex training and can be used on site i.e. where the products are needed rather than in specialist factories from which the products have to be transported to the sites at which they will be used, with the inevitable risk that the amount of product delivered will be too little or too much.

10 In a preferred form of our invention after the free gelling ions have been generated in the sol in the sol in the in-line mixer the sol is allowed to gel quiescently immediately after leaving the in-line mixer. Firstly, it is most unexpected that gelling ions can be generated in the alginate or low-methoxy pectate sol in an in-line dynamic mixer without the resulting gel being of poor quality. Secondly, The process has great advantages in terms of simplicity as we also explain elsewhere.

20 Normally the dispersion of alginate or low-methoxy pectate and the water are fed to one end of the mixer and the free gelling ions are generated downstream such that the sol of alginate or low-methoxy pectate is formed before the mixture comes into contact with the free gelling ions.

The free gelling agents are preferably generated using alternative b) indicated above i.e. by feeding a dispersion of a low-solubility salt providing gelling ions to the sol.

The dispersant used i.e. for the alginate or low-methoxy pectate, for the acid or for the low-solubility salt providing gelling ions is preferably an anhydrous liquid dispersant which disperses or dissolves in water.

- 5 The dispersant should preferably be such that the alginate or low-methoxy pectate, the acid or the low-solubility salt can remain in suspension in the dispersant over periods of up to fifteen minutes without stirring. The liquid dispersant should also preferably have lubricating
- 10 properties e.g. to be readily pumpable in conventional progressive cavity pumps; the type of pump which can conveniently be used for delivering the dispersed alginate or low-methoxy pectate or the low-solubility salt providing gelling ions to the in-line mixer. Such lubricating
- 15 properties are less important when piston pumps are used. Examples of suitable liquid dispersants are oils, glycerol and polyols. When the process is used to prepare a gel for feeding to livestock, the oil advantageously is an edible oil preferably containing lecithin e.g. a vegetable oil
- 20 containing about 10% lecithin. Water itself would produce a slurry which could not be pumpable in conventional progressive cavity pumps.

A feature of our invention is that there is reduced need to use calcium sequestrants.

- 25 In a specific form our process provides an advantageous system for preparing alginate or low-methoxy

pectate gels containing therapeutic amounts of biologically active substances, including but not limited to vitamins, enzymes and bacteria, especially those which are best kept in a protected environment e.g. dry or anaerobic till they  
5 are fed to patients or livestock.

In a special aspect of our invention such therapeutic amounts of biologically active substances can be incorporated in the dispersion of alginate or low-methoxy pectate or in the water or in the acid or in the dispersion  
10 of low-solubility salt providing gelling ions depending on the sensitivity of the active substance to water and to acid.

It is also convenient to incorporate other components in the dispersion of alginate or low-methoxy  
15 pectate, in the water or in the dispersion of salt providing gelling ions or in the acid fed to the sol to generate gelling ions. For instance this obviates the need for using very small dosing pumps. It also helps prevent settling out of the salt providing gelling ions.

20 An advantage of our process is that it can be performed at ambient temperature, in particular at low ambient temperatures i.e. at temperatures below 30°C especially below 20°C. Of course the temperature must be above freezing point e.g. above 0°C. Use of low  
25 temperatures helps avoid deterioration of active ingredients e.g. heat-sensitive ingredients such as



biologically active additives useful for optimal health and nutrition.

A further advantage of our process is that it can achieve the uniform incorporation of attractants which e.g. can substantially increase the probability of consumption by the livestock e.g. green colour for chicks and species-specific attractants in the fishing industry e.g. in fish farming. When being used to prepare gels for use in fish farming it is advantageous to include air when mixing the dispersion of alginate or low-methoxy pectate with the water and/or when mixing them with the calcium-ion generating system.

As mentioned above our process does not involve the use of complex systems or expensive equipment. Thus a further advantage of our process is that our process and equipment can be operated on demand and by relatively untrained people on site using minimal equipment and, without e.g. requiring the preservation of ingredients in an active state during transport and storage.

Our invention can particularly advantageously be used to produce an alginate or low-methoxy pectate gel containing a sensitive ingredient which requires an aqueous environment and which requires to be fed, e.g. to livestock, shortly, e.g. within 30 minutes, after being introduced to an aqueous environment. Indeed we have found, although the products of our process are

particularly advantageous in this respect, that alginate or low-methoxy pectate gels are excellent delivery media for such sensitive ingredients. Such gels deliver water, useful for the livestock and useful for certain biologically active materials e.g. bacteria but without excess free water, which can lead to problems e.g. hypothermia. Important examples of such sensitive ingredients are anaerobic bacteria and in a particularly important form of our invention a product is formed comprising anaerobic bacteria dispersed in alginate or low-methoxy pectate gel in which any water used is de-aerated water. For instance the water mixed with the dispersed alginate or low-methoxy pectate in our process contains dispersed anaerobic bacteria.

15       The water can be de-aerated by adding salts which generate carbon dioxide or simply by the addition of solid carbon dioxide in which the anaerobic bacteria have been delivered. The former is preferred because salts can be used which contain minor ingredients which are beneficial to the anaerobic bacteria.

20       The ratio of alginate or low-methoxy pectate to calcium can be adjusted to get adequate dryness with lack of significant syneresis and adequate strength. The process enables attainment of fast setting times e.g. within about 11 minutes of addition or production of the gelling ions. Adequate dryness is achieved by

increasing the amount of the alginate or low-methoxy  
pectate; adequate strength comes from increasing the level  
of salt providing gelling ions. Increasing the amount of  
salt providing gelling ions, without increasing the amount  
5 of alginate or low-methoxy pectate, will speed up the  
gelling rate and increase the gel strength but speeding up  
the gelling rate too much will increase syneresis.

Preferred sizes are particles of about 1 to 4 mm in  
maximum dimension but larger particles can be used if they  
10 are sufficiently friable.

As mentioned above alginate and low-methoxy pectate  
gels have been used to prepare meat products such as  
petfoods and to prepare simulated fruit products. Our  
process is a particularly simple and convenient way of  
15 making such products. The meat or fruit in pumpable form is  
advantageously included in the water used in the process  
but also can be included in the dispersion of alginate or  
low-methoxy pectate or in the dispersion of salt providing  
the gelling ions or in the acid fed to the sol to generate  
20 gelling ions.

Equipment according to the invention consists of an  
in-line dynamic mixer with feed points through which a)  
dispersion of alginate or low-methoxy pectate, b) water and  
c) a source of gelling ions e.g. a dispersion of a low-  
25 solubility salt providing gelling ions can be separately  
fed to the mixer, feed points a) and b) being sufficiently

spaced up-stream of feed point c) that in use the alginate or low-methoxy pectate forms a sol with the water before it comes into contact with gelling ions.

Dynamic mixers contrast with static mixers. In the latter the ingredients to be mixed are divided and mixed repeatedly. Dynamic mixers are a well-known class of mixers. An example of a dynamic mixer used in-line is the mini-Mondo mixer; it is a baffled turbine mixer. Such a mixer can be used in our process. However it was designed with aeration as a principal use and our process, although it can be used to prepare aerated products, is principally used to prepare non-aerated products.

The best way of defining the throughput speeds and mixing characteristics to be used in an in-line mixer for use in our invention is that they ensure formation of the sol before the gelling ions are generated. But a useful minimum tip speed of rotors is 1500 rpm. The sol is made the more quickly the higher the shear e.g. the higher the tip speed of rotors.

As mentioned above for convenience we describe our process and products initially in terms of the sodium form of alginate as a sol and gelation using calcium ions from salt providing gelling ions but that other cations can be used. Similarly we mention above that it is well-known that low-methoxy pectate has very similar characteristics to alginate.

"Low-methoxy pectate" is a well-known term. Normally low-methoxy pectates are considered to be pectates (i.e. pectins) containing less than 50% methoxylated carboxyl groups. For the process of this invention the low-methoxy pectate should preferably contain less than 30% methoxylated carboxyl groups.

As mentioned the sodium salt is a particularly convenient form of alginate or low-methoxy pectate from which to form a sol. The alginate or low-methoxy pectate used to form the products of the invention is preferably sodium alginate of high molecular weight (of the order of 100,000). Alginates having a low content of mannuronic acid residues (mannuronic: guluronic ratio less than 1:1) are especially suitable. The proportion of alginate or low-methoxy pectate used varies with its gelling ability (that is, the gel strength obtained per unit weight) and with the texture desired in the final product, in particular in the gel pieces. We have found that when the preferred sodium alginate is used it suitably forms from 0.4% to 4% by weight of the product formed. Other cations can be used to form sols with alginate or low-methoxy pectate e.g. potassium and ammonium.

Calcium sulphate (particularly in the dihydrate form) is the especially preferred low-solubility calcium salt to be used in the invention. However any salt providing gelling ions which has low solubility in water e.g. in the

aqueous sol can be used. Salts with a solubility less than 3.5% (weight percentages) are preferred, particularly preferably those with a solubility less than 1% and especially those with a solubility less than 0.3% but above  
5 a solubility of 0.02% e.g. calcium sulphate anhydrous, calcium sulphate dihydrate, calcium citrate and calcium tartrate. For some purposes a small amount, e.g. providing 2% of the calcium ions, of a soluble calcium salt such as calcium lactate can be included.

10 When the salt is a salt insoluble at neutral pH but soluble at acid pHs, preferred calcium salts include calcium citrate, calcium tartrate, calcium carbonate and calcium phosphates. Dicalcium phosphate dihydrate and dicalcium phosphate anhydrous are particularly preferred,  
15 especially dicalcium phosphate dihydrate.

It can be difficult to avoid the presence of some calcium ions in the water with which the alginate is mixed. But such presence of gelling ions is disadvantageous and at least 98% of the gelation of the alginate has to be due to  
20 the generation or addition of the gelling ions.

Our process, equipment and products will be now described by way of example with reference to Figures 1 and  
2.

Figure 1 is an overall flow diagram.

25 Figure 2 shows more detail of the gelling and dicing.

The quantities of ingredients were:

%  
(by weight)

Water feed:

5	De-aerated water	90
	Anaerobic bacteria plus minor ingredients	0.56

Alginate feed:

	Sodium alginate (Manugel DMB*)	3.50
10	Oil blend**	3.00

Calcium sulphate feed:

	Calcium sulphate dihydrate	0.80
	Chick feed	1.00
15	Oil blend	1.14
	Total	100

\* Trade Mark of ISP Alginates

\*\* Oil blend: Vegetable oil 90%, lecithin 10%

20

Sodium alginate is dispersed in vegetable oil containing 10% lecithin. Anaerobic bacteria, supplied as beadlets packed in solid carbon dioxide, are dispersed in deaerated water. The beadlets contain micro-ingredients to help activate and increase the growth rate of the anaerobic bacteria. The water was deaerated by adding salts which generated carbon dioxide.

The dispersion of sodium alginate in vegetable oil containing 10% lecithin and the dispersion of anaerobic bacteria in water were fed to an in-line dynamic mixer M1 by pumps P1 and P2 at rates 108.67 kg/hr and 7.8 kg/hr respectively. The mixer M1 was a 2kw mixer and was operated at 2800 rpm. It has nine rotators on a central shaft, each rotator bearing four equally spaced pins with a tip to tip diameter of 66mm. The central shaft has a diameter of 35mm. The pins rotate between stators. The water and the dispersion of sodium alginate were fed to the in-line dynamic mixer through inlets aligned with the first rotator.

Calcium sulphate was dispersed in oil together with milled chick feed and fed by pump P3 at 3.53 kg/hr to the in-line dynamic mixer M1 through an inlet aligned with pin 7. The alginate was hydrated i.e. in sol form by the time it reached pin 6 i.e. before being mixed with the calcium sulphate. The chick feed optimally contains a green colorant as this adds to the palatability of the product to chicks. The resulting mix was fed to moulds MD1 in which the alginate gelled quiescently. The moulds MD1 were set in a carousel C1 which rotated at 11 minutes per revolution. At stage 10 the mix which by that time had gelled was ejected by an ejector E1 into a Hobart dicer D1 where it was broken down into particles of 3 mm diameter. The product was attractive and beneficial to chicks.



CLAIMS

1. A process for preparing an alginate or low-methoxy pectate gel in which water and a dispersion of alginate or  
5 low-methoxy pectate are mixed in an in-line dynamic mixer to produce a sol of alginate or low-methoxy pectate and then free gelling ions are generated in the sol in the mixer either a) by including in the water or in the dispersion of alginate or low-methoxy pectate a salt  
10 providing gelling ions when dissolved which is insoluble at neutral pH but soluble at acid pHs and by feeding an acid to the sol as an aqueous solution or as a dispersion or b) by feeding a dispersion of a low-solubility salt providing gelling ions to the sol after which the resulting mixture  
15 is allowed to gel.
2. A process according to claim 1 in which after the free gelling ions have been generated in the sol in the mixer the sol is allowed to gel quiescently immediately after leaving the mixer.
- 20 3. A process according to claim 1 or claim 2 in which the free gelling ions are generated by feeding to the sol a dispersion of a low-solubility salt providing gelling ions.
4. A process according to any one of claims 1 to 3 in which a dispersant is used to prepare the dispersion of the  
25 alginate or low-methoxy pectate, of the acid or of the low-solubility salt which is an anhydrous liquid dispersant

which disperses or dissolves in water.

5. A process according to claim 4 in which the dispersant is such that the alginate or low-methoxy pectate, the acid or the low-solubility salt can remain in suspension in the dispersant over periods of up to fifteen minutes without stirring.
6. A process according to claim 4 or claim 5 in which the dispersant has lubricating properties.
7. A process according to any one of claims 4 to 6 in which the dispersant is an edible oil containing lecithin.
8. A process according to claim 3 and any one of claims 4 to 7 when dependent on claim 3 in which the low-solubility salt providing gelling ions has a solubility in the sol of less than 3.5%.
9. A process according to claim 8 in which the low-solubility salt providing gelling ions has a solubility in the sol of less than 1%.
- 10 A process according to claim 9 in which the salt has a solubility in the sol of less than 0.3% but above 0.02%.
11. A process according to any one of claims 8 to 10 in which the low-solubility salt providing gelling ions is a calcium salt.
12. A process according to claim 11 in which the calcium salt is calcium sulphate anhydrous, calcium sulphate dihydrate, calcium citrate or calcium tartrate.
13. A process for preparing an alginate or low-methoxy

pectate gel according to any one of claims 1 to 12 in which meat or fruit in pumpable form is included in one or more of the liquids mixed in the mixer.

14. A process for preparing an alginate or low-methoxy  
5 pectate gel according to any one of claims 1 to 12 in which therapeutic amounts of biologically active substances are included in one or more of the liquids mixed in the mixer.

15. A process according to claim 14 in which anaerobic  
10 bacteria are the biologically active substances and they are introduced into the mixer by incorporation into the water.

16. A process according to claim 14 or 15 in which the gel is broken into portions.

17. A product of a process according to any one of claims  
15 1 to 15.

18. A process in which a product of a process according to claim 14 or claim 15, after being broken into portions, is fed to livestock.

19. A process according to claim 18 in which the time  
20 between the incipiently gelling mixture leaving the mixer and the portions of gel being fed to livestock is less than 30 minutes.

20. A process according to claim 18 or claim 19 in which the livestock are chicks.

25 21. A feedstock for livestock which require water but are sensitive to free water in their environment consisting of

a product of claim 16.

22. A feedstock for chicks consisting of a product of claim 16.

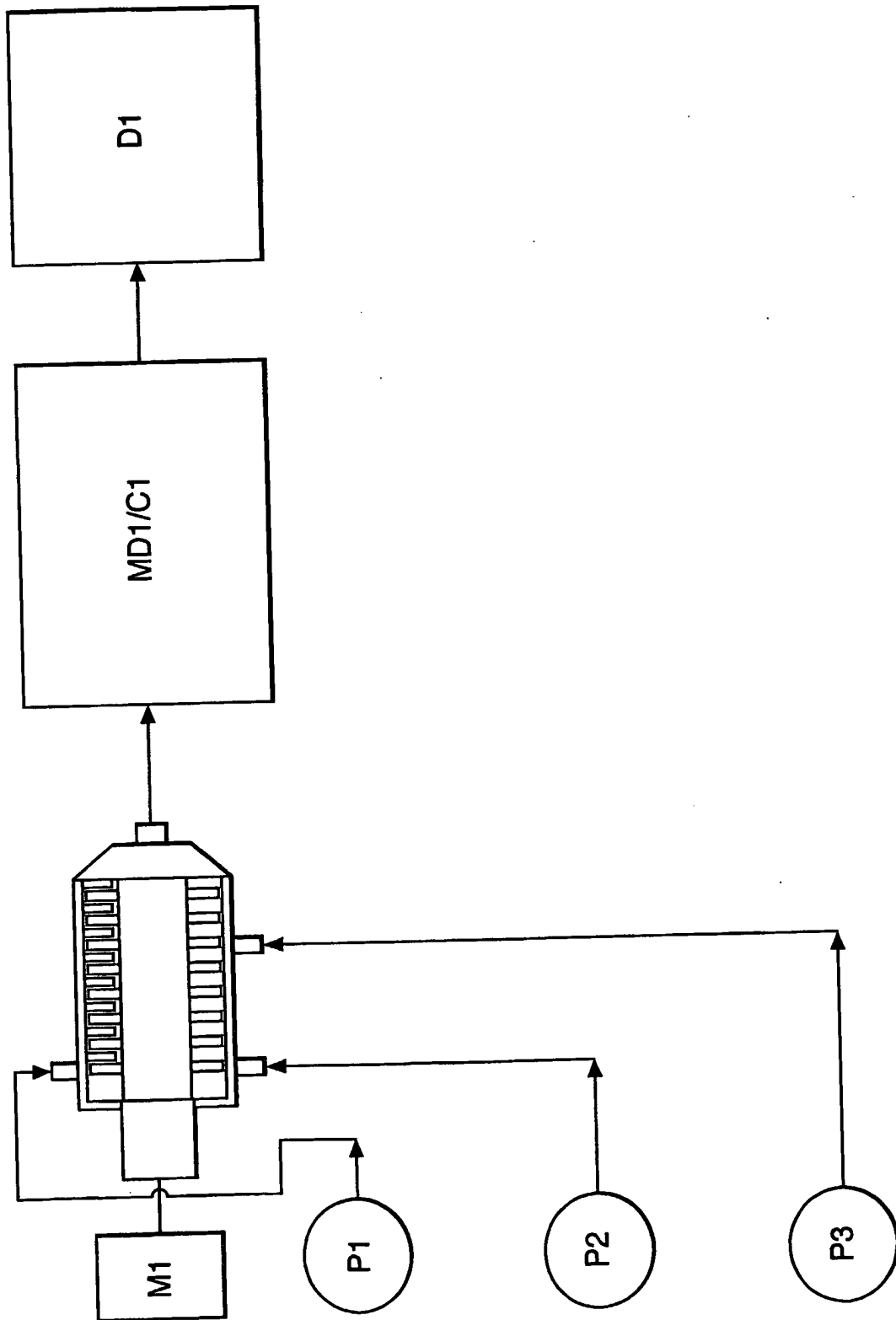
23. An in-line dynamic mixer with feed points through  
5 which a) a dispersion of alginate or low-methoxy pectate,  
b) water and c) a source of gelling ions can be separately  
fed to the mixer, feed points a) and b) being spaced  
sufficiently up-stream of feed point c) that in use the  
alginate or low-methoxy pectate forms a sol before it comes  
10 into contact with gelling ions.

24. Any new feature described herein or any new  
combination of herein described features.

25. A process or product substantially described herein  
with reference to the Example.

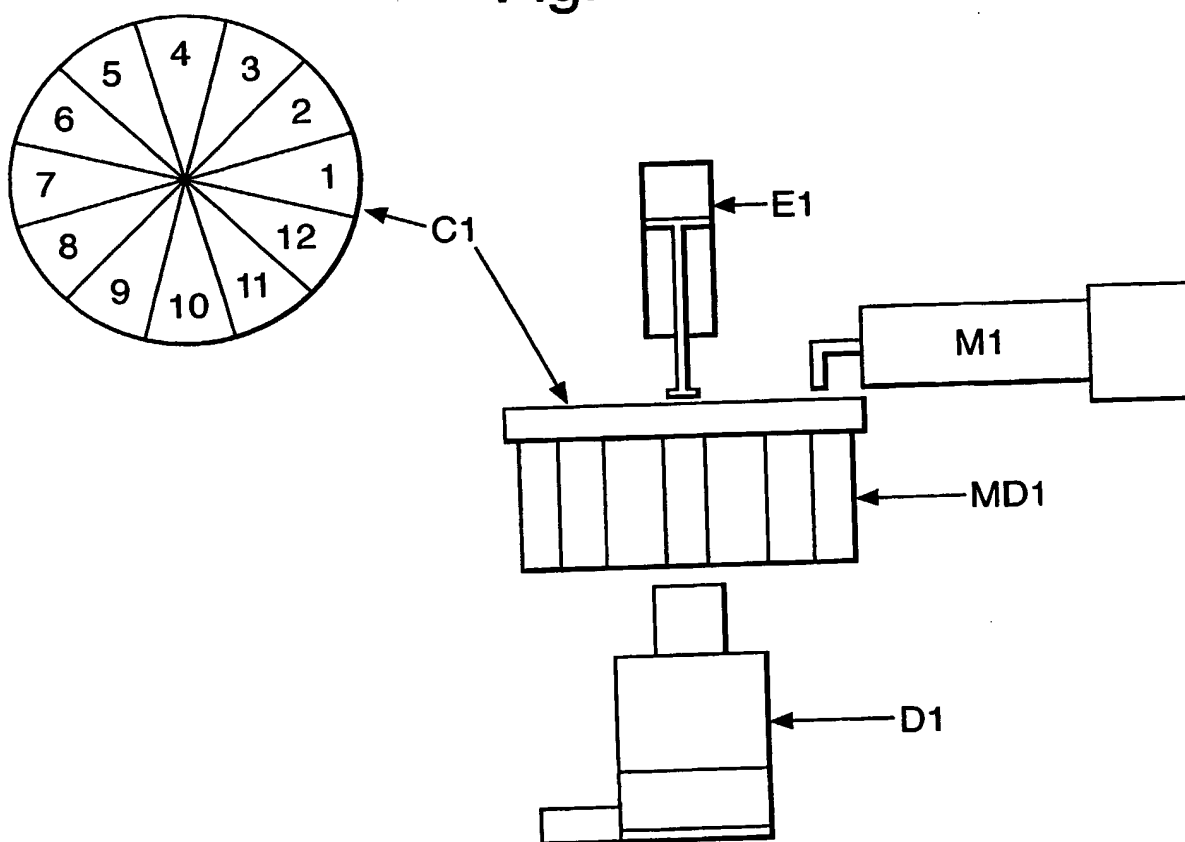
1/2

Fig.1.



2/2

Fig.2.



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 03/01657

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 A23L1/0524 A23L1/0532 A23K1/00 A23K1/18

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 A23L A23K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, BIOSIS, FSTA

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 02 056713 A (BARWICK BRYAN EDWIN ;KELLY THOMAS REID (GB); SAWANT VIJAY ARJUN (G) 25 July 2002 (2002-07-25) page 3, line 5 -page 4, line 26 example 1	17
A	page 2, line 24 page 3, line 5-7	1-16
X	US 4 624 856 A (SQUICCIARINI ALEX J ET AL) 25 November 1986 (1986-11-25)  column 3, line 61 -column 4, line 36 column 6-10 example 1  --- -/--	1-5, 8-12,16, 17

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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- \*P\* document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

29 August 2003

Date of mailing of the international search report

08/09/2003

Name and mailing address of the ISA

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 03/01657

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 369 198 A (UNILEVER LTD) 2 October 1974 (1974-10-02) page 1, line 10-54 page 2, line 1-64, 122-130 page 3, line 48 examples 1, 2, 5	17
A	page 1, line 17-19	1-16
X	US 4 348 418 A (SMITH JOHN R ET AL) 7 September 1982 (1982-09-07) column 2, line 16-48 column 3, line 67 -column 4, line 46 example 1	17, 21
A	column 2, line 40-42; example 1	1-16
X	US 4 347 261 A (CHALLENGER IAN A ET AL) 31 August 1982 (1982-08-31) column 1, line 29 -column 4, line 28 examples 1-5	17
A	column 1, line 35, 36	1-16
X	WO 93 03627 A (NOVUS INVESTMENTS LTD) 4 March 1993 (1993-03-04) page 2, paragraph 3 page 3; example 1	17
A	page 3, paragraphs 4, 5 example 1	1-16
X	US 5 217 740 A (LANIER KENT J) 8 June 1993 (1993-06-08) column 2, line 6-15 column 2, line 41-59 column 5, line 64 -column 6, line 5 claim 1	17, 21, 22
A	column 1, line 64	18-20
X	US 5 985 336 A (DIBNER JULIA J ET AL) 16 November 1999 (1999-11-16) column 2, line 40 -column 3, line 25 column 3, line 37-47 column 4, line 10-22, 52-67 column 5, line 26, 28, 61, 62 column 8, line 9-47 column 9, line 1-27 column 10, line 6-14	17, 21, 22
X	US 4 323 474 A (HANSEN NIELS H V ET AL) 6 April 1982 (1982-04-06) figure 1 column 2, line 26-34, 54-60	23
A	EP 0 574 051 A (MONDOMIX HOLLAND B V) 15 December 1993 (1993-12-15) figure 1	23



# INTERNATIONAL SEARCH REPORT

International Application No. PCT/GB 03 01657

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 24-25

The subject-matter of present claims 24-25 is not defined and therefore totally lacks clarity in the meaning of Art. 6 PCT. It would at best relate to an extremely large number of possible products or processes. In fact, the claims contain so many options, variables, and possible permutations that a lack of clarity within the meaning of Article 6 PCT arises to such an extent as to render a meaningful search of the claims impossible. Lack of support by the description for all the combinations mentioned in claim 24 is also an issue (Art. 6 PCT). Consequently, the search has been carried out for those parts of the application which do appear to be clear, namely claims 1-23 and claims 24-25 were not searched at all.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/GB 03/01657

## Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☒ Claims Nos.: 24-25  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 03/01657

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 02056713	A	25-07-2002	WO 02056713 A1	25-07-2002
US 4624856	A	25-11-1986	US 4444799 A	24-04-1984
			AU 560832 B2	16-04-1987
			AU 8639382 A	24-02-1983
			CA 1172096 A1	07-08-1984
			DE 3273609 D1	13-11-1986
			DK 300082 A	19-02-1983
			EP 0072758 A1	23-02-1983
			ES 8307457 A1	01-11-1983
			JP 1347097 C	13-11-1986
			JP 58031932 A	24-02-1983
			JP 61014771 B	21-04-1986
			JP 61108325 A	27-05-1986
			MX 7425 E	24-10-1988
			NZ 201611 A	11-10-1985
			ZA 8204825 A	27-04-1983
GB 1369198	A	02-10-1974	AT 339710 B	10-11-1977
			AT 486974 A	15-02-1977
			AT 326468 B	10-12-1975
			AT 982571 A	15-02-1975
			AU 3564271 A	17-05-1973
			BE 775405 A1	16-05-1972
			CA 1012833 A1	28-06-1977
			CH 563125 A5	30-06-1975
			DE 2156067 A1	18-05-1972
			DE 2167271 C2	07-08-1986
			ES 396968 A1	01-11-1975
			FR 2114706 A5	30-06-1972
			IE 35807 B1	26-05-1976
			IE 35808 B1	26-05-1976
			IT 1059805 B	21-06-1982
			LU 64270 A1	03-08-1972
			NL 7115640 A	18-05-1972
			NO 132890 B	20-10-1975
			SE 403426 B	21-08-1978
			SE 418672 B	22-06-1981
			SE 7700494 A	18-01-1977
			ZA 7107628 A	25-07-1973
US 4348418	A	07-09-1982	AU 6074180 A	05-02-1981
			BE 884573 A1	17-11-1980
			CH 645517 A5	15-10-1984
			DE 3028371 A1	19-02-1981
			DK 329980 A ,B,	02-02-1981
			FR 2462105 A1	13-02-1981
			IT 1131993 B	25-06-1986
			NL 8004205 A ,B,	03-02-1981
			NO 802132 A ,B,	02-02-1981
			SE 449550 B	11-05-1987
			SE 8005357 A	02-02-1981
			GB 2058539 A ,B	15-04-1981
US 4347261	A	31-08-1982	AT 2109 T	15-01-1983
			AU 537852 B2	19-07-1984
			AU 5064079 A	13-03-1980
			CA 1125085 A1	08-06-1982

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 03/01657

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4347261	A		DE 2964424 D1 DK 374979 A EP 0009897 A1 FR 2435211 A1 IE 48475 B1 JP 55058075 A ZA 7904679 A	03-02-1983 09-03-1980 16-04-1980 04-04-1980 06-02-1985 30-04-1980 29-04-1981
WO 9303627	A	04-03-1993	AU 2470292 A WO 9303627 A1 GB 2258800 A	16-03-1993 04-03-1993 24-02-1993
US 5217740	A	08-06-1993	NONE	
US 5985336	A	16-11-1999	US 5928686 A AU 723485 B2 AU 6153996 A CA 2222515 A1 CN 1191469 A CZ 9703821 A3 EA 1648 B1 EP 0831718 A1 HU 9900850 A2 JP 11506617 T NO 975691 A NZ 310705 A PL 323720 A1 SI 9620072 A SK 165097 A3 TR 9701559 T1 WO 9639862 A1 US 6329001 B1 US 6210718 B1 US 5976580 A ZA 9604883 A	27-07-1999 31-08-2000 30-12-1996 19-12-1996 26-08-1998 15-07-1998 25-06-2001 01-04-1998 28-07-1999 15-06-1999 05-12-1997 30-08-1999 14-04-1998 31-10-1998 09-09-1998 21-03-1998 19-12-1996 11-12-2001 03-04-2001 02-11-1999 07-01-1997
US 4323474	A	06-04-1982	EP 0011885 A1	11-06-1980
EP 0574051	A	15-12-1993	NL 9200826 A EP 0574051 A1	01-12-1993 15-12-1993